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APPARATUS FOR THE MEASUREMENT OF TRANSPORT PROPERTIES OF POLAR SEMICONDUCTORS

Martin M. Sokoloski and Felix E. Geiger
Goddard Space Flight Center
Greenbelt, Maryland

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SUMMARY

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The existing theoretical and experimental data on the mobilities of polar semiconductors are reviewed briefly, with special emphasis on PbTe because of its technical importance in thermoelectric power generation. Theoretical calculations on optical and acoustical mode scattering are compared with experimental data.

It is generally assumed, on the basis of experimental results, that the mobility follows a $T^{-5/2}$ law; however, experimental evidence indicates that the effects of changing statistics and possible changes in the effective mass as a function of temperature may hide the true dependence of the mobility on temperature. Therefore a new series of measurements of transport properties, such as the Hall coefficient and resistivity, is suggested; and apparatus to measure these properties in the range from 80° to 850°K is described. The apparatus consists of a cryostat in which the sample can be cooled to liquid nitrogen temperatures, and then heated and held at any desired intermediate temperature. A detailed description is given of the experimental apparatus: the cryostat, vacuum system, and sample holder assembly. The transport properties (Hall constant, resistivity, etc.) can be measured by the usual dc method; and, alternatively, an ac bridge can be used for direct resistance determination.

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INTRODUCTION

One of the most successful materials used in thermoelectric generators is PbTe, whose macroscopic properties are fairly well known but whose scattering mechanism—which determines the electron and hole mobilities and the carrier effective mass—is still uncertain because of the lack of experimental information and contradictory results. The calculation of the mobility of electrons and holes in PbTe is complicated by various scattering mechanisms apparently present at the same time. In ionic crystals, where the frequency spectrum has two branches, one optical and the other acoustical, both modes will contribute to the scattering of charged particles in the lattice. PbTe is believed to have substantial ionic bonding (Reference 1), and consequently scattering by optical modes is expected to contribute heavily to the total relaxation mechanism of the crystal.

The interaction of the electron or hole with the lattice consists of an absorption from, or emission to, the lattice of a single phonon. The laws of conservation of momentum and energy dictate that the phonon energy is smaller than the electron energy and that the phonon momentum is smaller than twice the electron momentum. As a consequence, only longwave phonons will take part in the collisions. The average number of phonons of a given wavelength increases with temperature; hence scattering by both optical and acoustical modes will be important only at elevated temperatures. At low temperatures the interaction of carriers with point imperfections, such as ionized impurities and others (i.e., dislocations), becomes important. We shall briefly review the theoretical situation on mobility calculations and make comparisons with some of the published data on PbTe.

It is generally agreed, on the basis of experimental results, that the temperature dependence of the mobility in PbTe follows a $T^{-5/2}$ law over a broad temperature range, 100° to 500°K (Reference 2); however, considerable experimental variations from this power law have been reported and will be discussed below. The $T^{-5/2}$ law for the mobility μ departs significantly from the theoretical calculations. Theory predicts for *acoustical* scattering and nondegenerate statistics that $\mu \propto T^{-3/2}$ (Reference 3a). Scattering of carriers by the *optical* modes of lattice vibrations for a nondegenerate system is characterized by a $T^{-1/2}$ dependence (Reference 3b) of the mobility for temperatures T greater than a characteristic* temperature θ; for temperatures less than θ, and nondegenerate statistics, the mobility (Reference 3c) is given by $\mu \propto \exp(\theta/T)$. Attempts to fit the PbTe mobility data to the optical mode scattering calculations have been singularly unsuccessful — a fit could be obtained only by assuming a very high Debye temperature, 1100°K (References 3d and 4).

Impurity scattering is expected to become important at low temperatures when the average energy of the electrons is low. Calculations based on a Rutherford-type scattering analysis yield a mobility proportional to $T^{3/2}$ (Reference 3d). Experimental evidence for impurity scattering at low temperatures is, as in the case of lattice scattering, rather ambiguous. Results by Allgaier and Scanlon (Reference 5) in the temperature range from room temperature to 4.2°K fail to reveal mobilities limited by impurities, whereas Stavitskaia and Stil'bans (Reference 6) find considerable evidence for impurity scattering at temperatures below 200°K—without, however, considering the effects of degeneracy. The degeneracy temperature for PbTe with an impurity concentration on the order of $10^{18}/cm^3$ is about $42/m^*$ or 170°K; this implies changes in the observed Hall effect and calculated mobility due to changes in statistics below the degeneracy temperature (Reference 5). Further examples of disagreement on experimental data can be seen in the results of Devyatkova and Smirnov (Reference 7) and Gershtein, Stavitskaia, and Stil'bans (Reference 8), all of which reveal some dependence of mobility on carrier concentration in the temperature range from 100°K to several hundred degrees above room temperature. Data by Shogenji and Uchiyama (Reference 2) on PbTe, and Petritz and Scanlon (Reference 9) on the homologous compound PbS, show independence of carrier concentration in the same temperature range, indicating that the mobility is not limited by ionized impurities.

Even larger deviations from the predicted results (i.e., either for acoustical or optical mode scattering) are reported by Kolomoets, Stavitskaia and Stil'bans (Reference 10) who find a T^{-3} dependence for the mobility in the 300° to 700°K temperature range. This, however, seems to be exceptional and has not been reported by anyone else. In one of the most recent papers on this subject, Devyatkova and Smirnov (Reference 7) confidently assert that their data, after correction for changes in statistics at low temperatures, definitely confirm acoustical scattering in PbTe. In the face of such bewildering results, it is difficult to be very confident; and it is furthermore difficult to understand why other investigators, who have made corrections for degeneracy, arrived at such divergent results.

Interestingly enough, all theoretical calculations for lattice scattering, both acoustical and optical, do include a strong dependence on the effective mass of the carriers (i.e., $m^{*-5/2}$ and $m^{*-3/2}$ respectively). Yet very little effort has been spent on the problem of finding out how m^* varies as a function of temperature. This is clearly a problem of considerable importance if the true dependence of the mobility on temperature is to be determined. Only Miller, Komarek, and Cadoff (Reference 11) and Smirnov, Moizhes, and Nensberg (Reference 4) have taken the temperature variation of the effective mass into consideration. The latter's work on PbSe shows m^* to vary as $T^{0.45}$ and $T^{0.35}$ for holes and electrons respectively. If this temperature variation is taken into consideration in conjunction with the experimentally observed $T^{-5/2}$ law for the mobility, the temperature variation of the mobility can be

*The characteristic temperature is defined by $\hbar\omega_0/k$, where it is assumed that the polarization waves have a single fixed vibrational frequency ν_0.

explained in terms of acoustical scattering. Unfortunately Miller, Komarek, and Cadoff (Reference 11) found no such temperature dependence of m^* for PbTe in roughly the same temperature range.

Clearly, a more comprehensive and unified investigation is needed to clarify the importance and influence of all effects, such as change in statistics with temperature and concentration, the temperature dependence of the effective mass, sample preparation (single crystal or polycrystalline), and perhaps types of carriers. Only when all these factors are considered in unison will it be possible to make an intelligent decision as to the type of scattering predominating in PbTe and other homologous ionic (polar semiconductors).

This report describes an apparatus (Figure 1) and techniques for measuring the Hall constant, resistivity, and possibly—with some modification—magnetoresistance and the thermoelectric power of semiconductors, specifically PbTe. The purpose of these measurements is to determine the mobility and effective mass, and to establish with some certainty the mechanism of scattering that determines the flow of charges.

DESCRIPTION OF APPARATUS

Material and Construction

This Hall apparatus is a modification of a similar type employed quite recently (Reference 12), except that the operational temperature range for this cryostat is from 77° to 850°K rather than 77° to 400°K. As shown in Figure 2, all parts are made of brass except the outside and inside tubing, which extends between the pole pieces of the magnet (detail A, Figures 2 and 3). All parts and joints of the apparatus are silver-soldered for structural strength and then soft-soldered for vacuum tightness. The inner tube can be removed at will from the entire assembly, since it is connected to an O-ring flange, which in turn is bolted to the brass part as shown in Figure 2. Another inner vacuum tube is being constructed with the bottom part welded, in anticipation of attaining a still higher terminal temperature. Both tubes are made of Inconel, which has a relatively low thermal conductivity, is nonmagnetic, and is structurally sound at these high temperatures.

A custom-made Dewar is used to cool down the outside of the tubes shown in Figure 2. A magnet and power supply capable of maintaining a 7 to 8 kilogauss field with 2 inch pole pieces at a gap of 2 inches is employed. To facilitate the removal of the entire Hall apparatus from the magnet, the entire assembly described below is mounted by means of lattice clamps and rods on a movable platform.

Inert Gas System

A schematic drawing of the entire vacuum and gas system is shown in Figure 4. The two larger valves are 1-1/8 inch high-vacuum valves, while the valves in the gas system are high

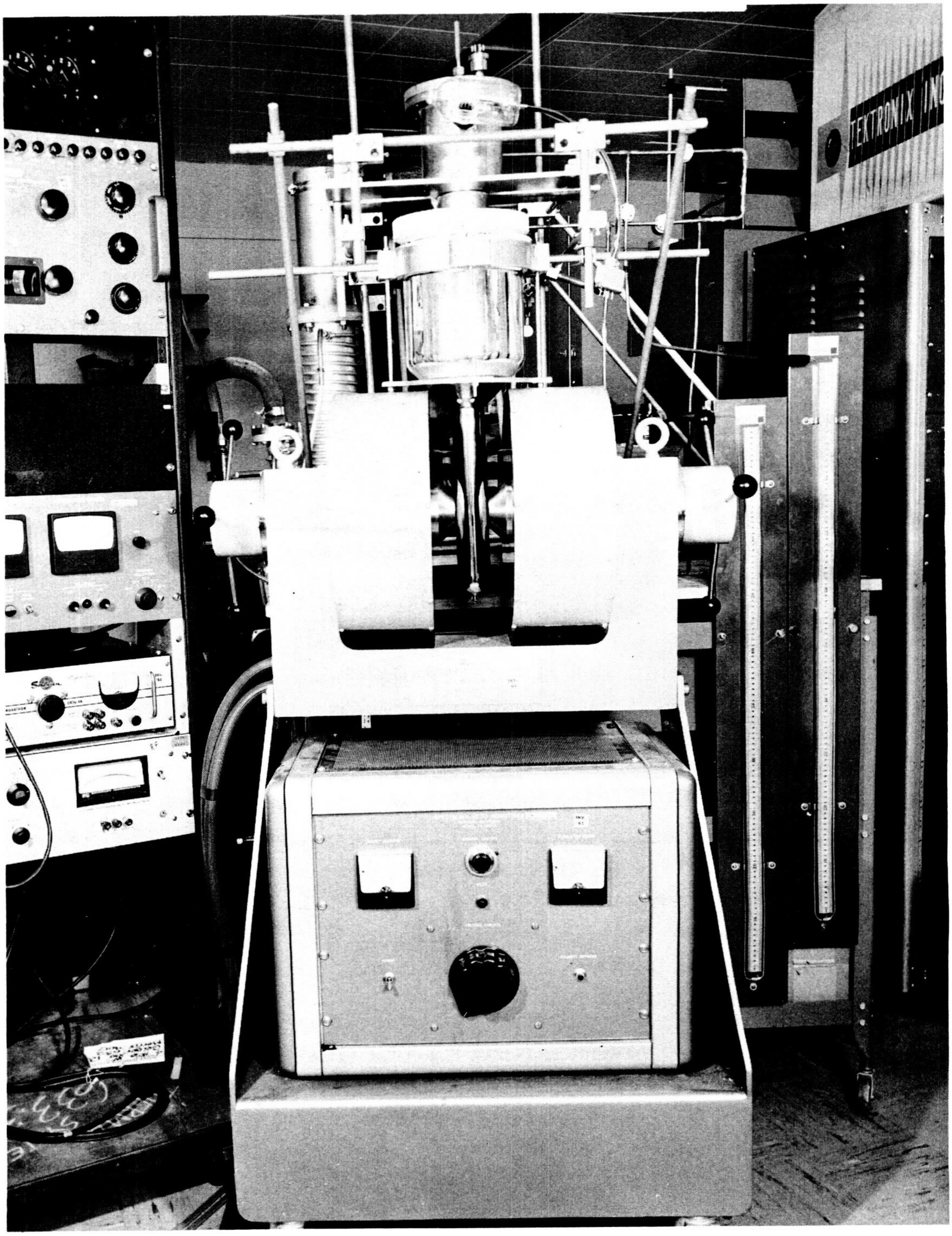

Figure 1—The apparatus.

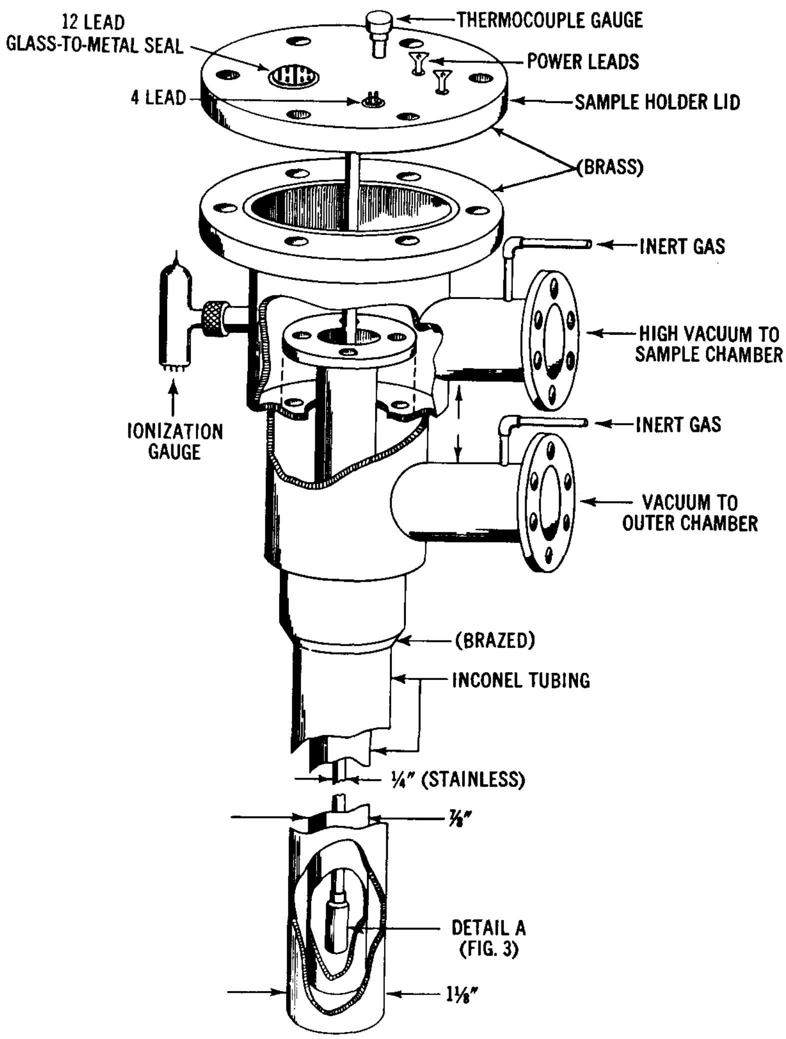

Figure 2—Hall cryostat.

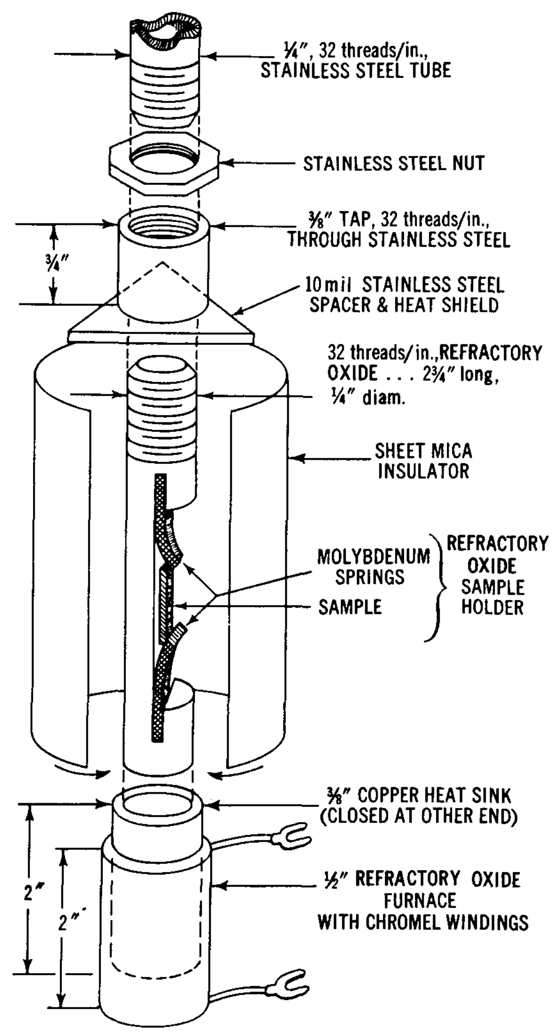

Figure 3—Sample holder assembly.

to low pressure valves. As indicated, an inert gas atmosphere can be introduced into one or the other chamber, or both.

This introduction of inert gas into the chambers serves several purposes. At 77°K the inert gas in the outer and inner chambers maintains a heat exchange between the sample and the liquid nitrogen bath surrounding the outer tube. Then, by regulating the gas pressure and the furnace current, any temperature between the liquid bath and room temperature can be reached and maintained. In practice, it is advantageous to measure in the direction of increasing temperature (i.e., initially both tubes are filled with an inert gas, the furnace is *off*, and the entire assembly is immersed in the liquid nitrogen bath). In the high temperature region the outer chamber is completely evacuated to avoid heat loss by conduction. Radiation losses through the sides are minimized by using molybdenum radiation shields. Also, irreversible effects at high temperatures, which characterize some semiconductors such as the lead salt compounds (Reference 13), can be minimized by subjecting the inner sample chamber to an inert gas pressure. Since impurities and traces of oxygen can easily contaminate the sample, the gas used is of the water pumped type and is passed through a dryer before entering the inner chamber.

If necessary, the system can be easily modified so that each chamber has its own independent inert gas supply.

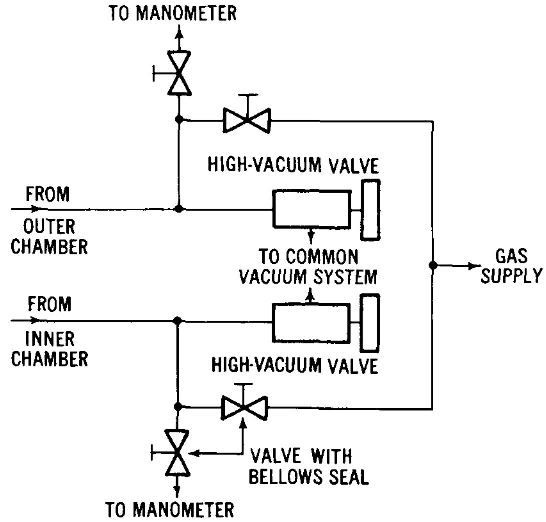

Figure 4—Vacuum and inert gas system.

Vacuum System

The vacuum system uses a diffusion pump with a pumping speed of 320 liters/second, joined to a vented exhaust forepump. The ultimate pressure capability of the diffusion pump is 5×10^{-7} torr (mm of Hg). So far, a pressure of 8×10^{-7} torr has been attained with both pumps and without a cold trap. A high pumping speed is needed, since some of the elements in the sample chamber (Figure 3) outgas rather heavily. Presently, both chambers are evacuated by the same pumps. However, with a slight modification each chamber can have its own individual pumping system.

Lid Assembly and Sample Holder

The lid, the 1/4 inch sample holder rod, and the sample holder itself (shown in Figure 3) are designed to be one integral part. For easy access to the sample, all that needs to be removed is the lid. This type of lid design has another advantage in that it can be readily adapted to magnetoresistance measurements by connecting the 1/4 inch sample holder rod to a rotary vacuum seal soft-soldered into the lid.

The most important part of the apparatus is the refractory oxide sample holder shown in Figure 3. The advantage of this refractory material, aside from its high resistivity ($2 \times 10^{9}\,\Omega$/cc at 570°K), is its ability to be free-machined. Since molybdenum is a satisfactory spring material over the temperature range in consideration, it is used not only to secure the sample to the holder but also to act as pressure current contacts. The current contacts completely cover the ends of the sample to insure a uniform field through most of the sample. Because of the temperature range concerned, various soldering (Reference 14) and electroplating (Reference 15) methods for making ohmic contacts to the sample for Hall and resistivity probes are out of the question. The capacitor discharge method (Reference 16) is the most successful and consists of discharging a capacitor through a 0.001 to 0.002

inch diameter platinum wire in contact with the sample. The heat generated welds the probe to the sample without damage. As a result of the small cross-sectional area in contact with the sample, contamination due to diffusion is small compared with that due to other methods. The probes are placed far enough from the current contacts, in case there is unequal contact of the current probes with the sample, so that they "see" a uniform electric field. Chromel-Alumel thermocouples placed under the sample prove adequate for the temperature range.

Surrounding the sample holder and insulating the leads from the copper heat sink is a thin sheet of mica. The heat sink, which eliminates thermal gradients and insures uniform heating of the sample, slips directly over the sample holder; and over this slips the furnace tube wound with #26 Chromel wire. Like the sample holder, the furnace is also made of a refractory oxide material. A modified heater can also be slipped over the sample holder to produce longitudinal thermal gradients in the sample. As a result, the thermoelectric power and other galvanomagnetic effects can be measured as a function of temperature.

Sample Preparation

Lead salt samples with a length-to-width ratio of over 3 to 1, to suppress shorting-out of the Hall field due to the current electrodes (Reference 17), are cut from a polycrystalline ingot by means of a diamond saw. These samples are etched with a dilute solution of equal parts of HCl and HF. To determine effectively the band gap energy, measurements are needed on single crystals (Reference 18). These crystals require delicate handling, since evidence shows that point defects and other dislocations can be created to affect the mobilities of the carriers at low temperatures (References 5 and 19). Nevertheless, a large portion of surface dislocations can still be removed by etching.

DC MEASUREMENT OF THE HALL VOLTAGE AND CONDUCTIVITY

When a magnetic field is applied perpendicularly to an electric field, all charge carriers in the sample experience a Lorentz force that gives rise to a "Hall" field perpendicular to both the magnetic and electric fields. Two probes directly across from each other should suffice to pick up this voltage. However, as is shown in Figure 5, the three-probe method is employed to eliminate any angular dependence of the Hall voltage due to misalignment of the probes.

The Heli-pot potentiometer is adjusted so that zero voltage is read when no magnetic field is applied; this puts a "virtual" probe on an equipotential line with the other probe. The magnetic field is turned *on* and the resulting voltage, which is one-half the Hall voltage, is measured. This procedure is necessary since any voltage due to misalignment of the probes may exceed the "true" Hall voltage. Two of the three probes in this three-probe method act as the resistivity probes. The distance between these two probes in this three-probe method act as the resistivity probes. The distance between these

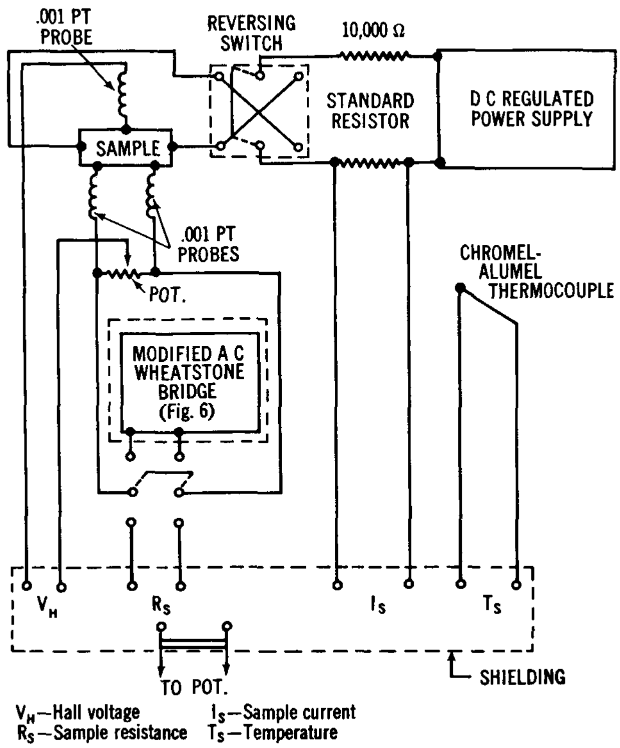

Figure 5—DC measuring circuit.

two probes is measured with a micrometer slide microscope. The current is supplied through a high impedance circuit, a dc current regulated power supply in series with a high wattage resistor. This minimizes any spurious resistance effects between the sample and the molybdenum pressure contacts. The sample current is simply obtained by measuring the voltage drop across a standard resistor. Since the contact resistance of the probes may exceed the bulk resistance of the sample, all voltages are measured with a high precision potentiometer.

To eliminate any unwanted thermoelectric effects, an average of two readings for the resistivity measurements is obtained by quickly reversing the current. Errors introduced by temperature gradients in the sample can be reduced in the Hall measurement by taking an average of four measurements obtained with the fields in different directions. The Ettingshausen effect, which is an inherent error in this type of measurement, is so small as to be negligible.

AC MEASUREMENT OF THE CONDUCTIVITY

The measurement of the conductivity of semiconductors with large thermoelectric powers is complicated by the Peltier effect. The current through the sample produces a temperature gradient across it, which in turn gives rise to a Seebeck voltage. In the potential probe dc method (Reference 20), conductivity measurements are made by quickly reversing the current and taking the average of two voltage readings. These complications can be avoided by using an ac method introduced by Goldsmid (Reference 21). This method uses a modified ac Wheatstone bridge, which will measure directly the resistance of a sample between two potential probes by a null method. Thus, contact resistances as well as nonohmic contacts do not enter the resistance determination.

Figure 6 is a circuit diagram of the bridge. An audio generator supplies alternating current to the bridge; P and Q are two decade resistance boxes of 10,000 and 1000 ohms respectively, which may be used up to several hundred cycles per second. As the null detector, an electronic detector was chosen in preference to the usual ac galvanometer. The instrument is essentially a "twin T" tuned ac amplifier with a sensitivity of roughly 0.5 microvolt per scale division of output meter. Different "twin-T" plug-in units allow different frequencies to be used. To avoid 60 cycle interference and reactance effects, an operating frequency of 50 cycles was chosen. A higher frequency is more desirable to avoid 60 cycle interference but will aggravate problems of pickup from adjacent circuit elements, and thus make a null reading more difficult.

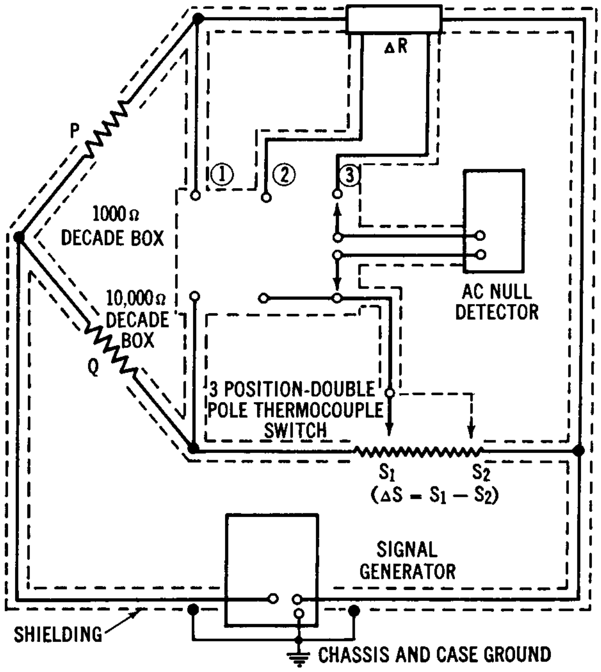

Figure 6—Modified Wheatstone bridge circuit.

In preliminary measurements, a 25 ohm Helipot was used for the "slidewire." The resistance of the "slidewire" can be obtained quite readily from the Helipot dial reading—this proved surprisingly accurate—making possible measurements in the range from 0.01 to 10 ohms with an accuracy considerably better than 1 percent. To avoid possible difficulties with resistance nonlinearities and recalibration, the Heli-pot was replaced by a Kohlrausch slidewire. The bridge is readily balanced, and the balance is quite sharp. With an input to the bridge of roughly 2 to 3 volts, the residual voltage at balance is on the order of 5 to 10 microvolts, which is in large part made up of 60 cycle pickup and residues from the impure waveform put out by the signal generator. The whole circuit floats above ground, including the null detector and null detector chassis. It seems to make little difference whether the case of the detector is grounded or not. All connections between bridge elements are carefully shielded and grounded to the signal generator ground. The signal generator output itself floats.

Three null measurements must be made to determine the resistance ΔR of the sample. With the three-position switch (see Figure 6) in position 1, the ratio of resistances P and Q is adjusted to give a null reading. Leaving P/Q fixed, null readings are obtained for positions 2 and 3 with the slidewire. It can be shown that the sample resistance between the potential probes is given by $\Delta R = \Delta S\ (P/Q)$, where ΔS is the difference in the slidewire readings of the balance positions 2 and 3.

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